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Interfacial and Electrokinetic Characterization of IPA Solutions Related to Semiconductor Wafer Drying and Cleaning

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In this study, the interfacial and electrokinetic phenomena of mixtures of isopropyl alcohol (IPA) and deionized (DI) water in relation to semiconductor wafer drying is investigated. The dielectric constant of an IPA solution linearly decreased from 78 to 18 with the addition of IPA to DI water. The viscosity of IPA solutions increased as the volume percentage of IPA in DI water increased. The zeta potentials of silica particles and silicon wafers were also measured in IPA solutions. The zeta potential approached neutral values as the volume ratio of IPA in DI water increased. A surface tension decrease from 72 to 23 dynes/cm was measured when the IPA concentration increased to 30 vol %. The surface excess of IPA at the air–liquid interface reached a maximum at around 20 vol % IPA. The adhesion forces of silica particles on silicon wafers were measured using atomic force microscopy in IPA solutions. The adhesion force increased as the volume percent of IPA in water increased. Lower particulate contamination was observed when the wafers were immersed and withdrawn from solutions containing less than 25 vol % IPA.
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Wet chemical processes are indispensable in wafer cleaning due to their effectiveness in removing contaminants. Recently, wet cleaning and drying have become more important than ever due to increases in pattern density and wafer size and rapid decreases in pattern sizes below 0.13 μm. Spin and hot isopropyl alcohol (IPA) vapor drying have been displaced by Marangoni-type IPA drying,[1] which utilizes the surface pressure gradient at the air–liquid interface at room temperature.

IPA has been utilized in wet cleaning and drying to increase the surface wettability and to enhance wafer drying because of its low surface tension, high vapor pressure, and high solubility in water.[2,3] Even though studies evaluating a thin IPA layer on deionized (DI) water have been performed in order to elucidate the wafer drying phenomena,[4,5] few studies have been conducted evaluating the interfacial and electrokinetic phenomena of IPA solutions from the point of view of semiconductor wet processing. In this study, electrokinetic and interfacial characterization of IPA solutions was conducted in order to elucidate the role of IPA in solutions in semiconductor cleaning and drying processes.

Experimental

Pure IPA (semiconductor grade, Dongwoo Fine Chemicals Co.) was mixed with ultrahigh-purity DI water and left for 5 h in a closed system for complete mixing. In order to characterize the properties of the mixture of IPA and DI water, the viscosity and surface tension of the mixed solutions were measured as a function of IPA concentration using a viscosity meter (Brookfield DV-II, Brookfield Engineering Laboratory, Inc.) and a Wilhelmy-type[6] surface tension analyzer (DCA 315, Cahn Co.), respectively, at room temperature.

Fumed silica (<50 nm, Degussa Co.) particles were used for measuring its zeta potential and particle size. The zeta potential and mean particle size were measured by a laser electrophoretic zeta potential analyzer (LEZA-600, Otsuka Electronics Co.) at various concentrations of IPA solution. Silicon particles (−325 mesh, 99.9%, Sigma-Aldrich Co.) were used to measure the zeta potential instead of the Si wafer surface.

The adhesion force between a silica particle and the Si surface was measured using atomic force microscopy (AFM, AutoProbe CP Research, PSIA Co.) at different concentrations of IPA solutions.[7,8] A 40 μm diam spherical soda lime silica particle (Duke Scientific Co.) was attached on a Si_3N_4 tipless cantilever. Silicon wafers were precleaned in SPM ($H_2SO_4 \cdot H_2O_2$ = 4:1 vol %, 120°C) and APM ($NH_4OH \cdot H_2O_2 : H_2O$ = 1:1:5 vol %, 80°C) cleaning solutions for 10 min. After cleaning, the wafers were rinsed using DI water for 3 min. Then the wafers were finally cleaned with dilute hydrofluoric acid solution (0.5% DHF) for 5 min and rinsed with DI water.

Six-inch wafers were used for the drying and particle adhesion experiments in various concentrations of IPA solutions. The wafers were dipped into the IPA mixtures contaminated with silica particles (0.5 μm, Duke Scientific Co.) for 2 min 30 s. After dipping, the wafers were withdrawn very slowly at a speed of 2.4 mm/s. The wafers were dried by hot N_2 blowing. The number of particles on the wafer surfaces was measured using a laser particle scanner (Surfscan 5500, KLA Tencor Co.) before and after drying the wafers.

Results and Discussion

Zeta potential is an important variable for estimating the electrostatic interaction of a particle with the wafer surface during wet cleaning processes. Zeta potential (ζ) is a function of viscosity (η), dielectric constant (ε_r) of the medium, applied electric field (E) and mobility (υ) of a particle, as shown in Eq. 1

$$\zeta = \frac{\eta \upsilon}{\varepsilon_0 \varepsilon_r E} \quad [1]$$

It is necessary to measure the viscosity and dielectric constant of an IPA solution in order to calculate the zeta potential of particles at different concentrations of IPA. The dielectric constant linearly decreased as the concentration of IPA is increased in DI water, as shown in Fig. 1.[9] The viscosity of an IPA solution was measured as a function of IPA concentration as shown in Fig. 2. The viscosity increased until the amount of IPA in the mixture reached 50 vol %, then the viscosity decreased.

Figure 3 shows the zeta potential of silica and silicon particles with increasing IPA concentration. The zeta potential approached neutral values as the concentration of IPA reached 50 vol %. This indicates that the surface charge becomes neutral in IPA solutions. Previous studies have shown that IPA solutions effectively prevent and remove static charge buildup at IPA concentrations over 20 vol %.[2,10] The dispersion and stability of particles in liquids are strongly dependent on the zeta potential of particles. Figure 4 shows the change in the mean particle size of fumed silica particles as a function of IPA concentration. The mean particle size increased from 1000 to 1800 nm with increasing IPA concentrations. The interaction force between a particle and the Si surface can be measured by an AFM as the cantilever approaches the substrate.[7,8] Figure 5

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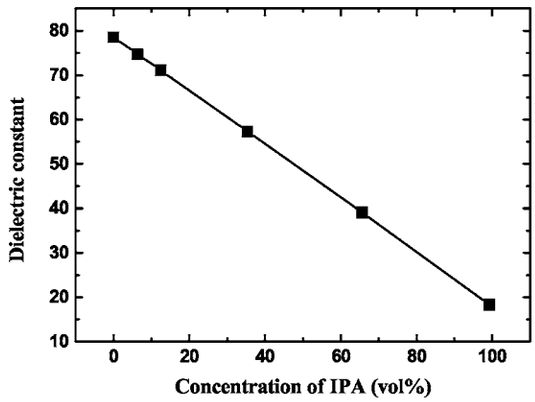

Figure 1. Dielectric constant of the mixture of DI water and IPA as a function of IPA concentration.

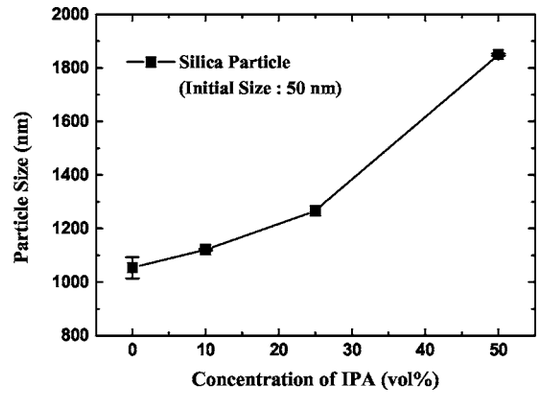

Figure 4. The change in mean particle size as a function of IPA concentration.

shows a typical force vs distance curve approach that was used in the experiments. In AFM, the surface of a sample is probed using a sharp tip that is several micrometers long and often less than 10 nm diam. Forces between the tip and the sample surface can cause the cantilever to bend or deflect. A detector measures the cantilever deflection as the tip scans the surface of the sample. From the force vs distance curve, the magnitude of interaction between two surfaces can be evaluated. Figure 6 shows the measured adhesion force between a spherical silica particle and Si surfaces. In DI water, silica showed the lowest adhesion force with the Si surface. The adhesion force increased as the IPA concentration increased.

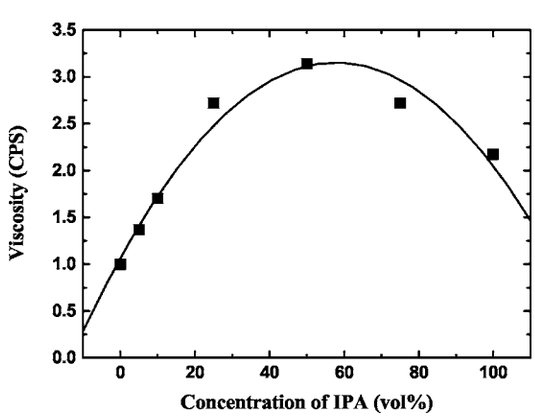

Figure 2. Viscosity of IPA solutions as a function of IPA concentration.

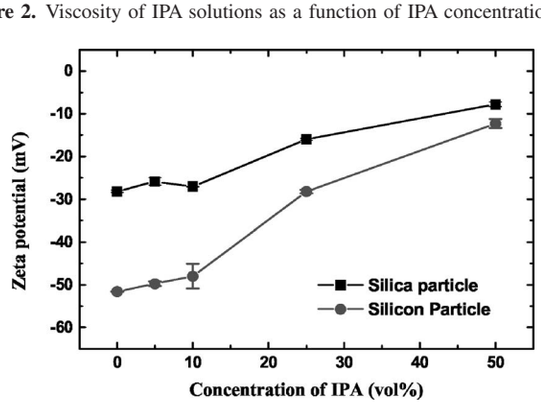

Figure 3. Zeta potentials of silica and silicon particles as a function of IPA concentration.

The Delaguin-Landaw–Verwey–Overbeek (DLVO) theory[11,12] estimates the repulsive and attractive forces resulting from the overlap of electric double layers and London-van der Waals force, respectively, as a function of interparticle distance. The total interaction force (V_T) occurring between the particles and the wafer surface in the solution is the sum of van der Waals force (V_A) and the electrostatic force (V_R), as shown in Eq. 2

$$V_T = V_A + V_R \quad [2]$$

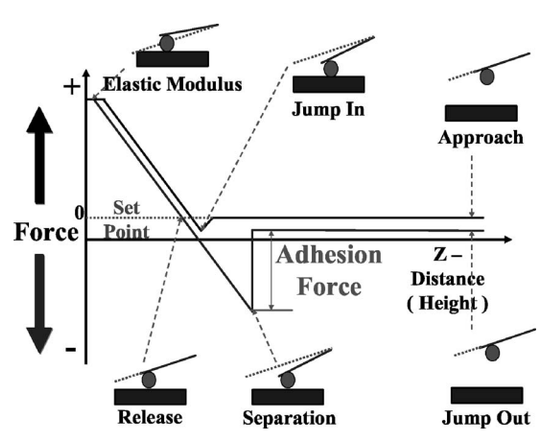

Figure 5. Force–distance curve and cantilever shapes as a function of applied force on a cantilever.

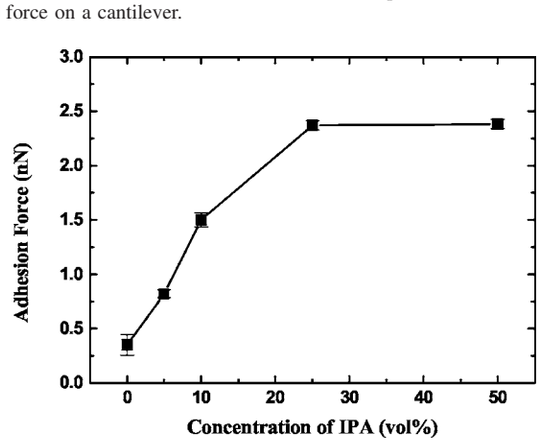

Figure 6. Adhesion force between a silica particle and the Si wafer surface at various concentrations of IPA.

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Table I. Hamaker constants of experimental materials.

Materials	Si	SiO_2	Water	IPA
A_{11} ($\times 10^{-20}$ J)	25.6[a]	6.5[a]	4.35[a]	4.2[b]

[a] Reference 15.
[b] Assumed as Hamaker constant of acetone.

If a small interparticle surface separation (H_0) is assumed, the van der Waals force between a spherical particle and a substrate can be expressed as shown in Eq. 3

$$V_A = -A_{123}\frac{R}{6H_0^2} \quad [3]$$

where, A_{123} is the Hamaker constant for surfaces 1 and 3 in a dispersion medium 2 and is calculated based on an A_{11} value, and R is the radius of a sphere. Equation 4 [13] represents a calculation of A_{123} from A_{11}, A_{22}, and A_{33}

$$A_{123} = (A_{11}^{1/2} - A_{22}^{1/2})(A_{33}^{1/2} - A_{22}^{1/2}) \quad [4]$$

The Hamaker constant can be expressed as a function of the ionization potential of the material.[14] The ionization potential of IPA has a value between those of water and acetone, and the Hamaker constants of acetone and water are almost the same. Because the Hamaker constant of IPA is not available, the Hamaker constant of acetone was used for the van der Waals force calculation. The Hamaker constants used in this study are summarized in Table I.

The calculation of the electrostatic force is more complicated due to the overlapping of the diffused double layers between the two surfaces. This calculation must rely on numerical solutions or various approximations. Overbeek's approximation[16] was used for the calculation of the electrostatic force due to a zeta potential larger than 25 mV on the surfaces, as shown in Eq. 5

$$V_R(H) = \frac{64\pi\varepsilon R k^2 T^2 \gamma_1\gamma_2}{e^2 z^2}\exp[-\kappa H] \quad [5]$$

where

$$\gamma = \frac{\exp[ze\psi_d/2kT] - 1}{\exp[ze\psi_d/2kT] + 1}$$

and, R is the particle radius, ε the permittivity of medium, k is the Boltzmann constant, T is absolute temperature, z the valance number, κ the reciprocal of Debye length, H is the distance between the surface and the particle, and ψ_d is the zeta potential of the particle and surface.

Figure 7 shows the calculated DLVO total interaction force between spherical silica and the Si surface as a function of the separation distance in an IPA solution. The theoretical interaction force of a silica particle agreed well with the trend of the AFM measured adhesion force as a function of IPA concentration. As the concentration of IPA increases, the attractive interaction becomes dominant between a silica particle and a silicon wafer. The largest repulsive forces were calculated in DI water without IPA.

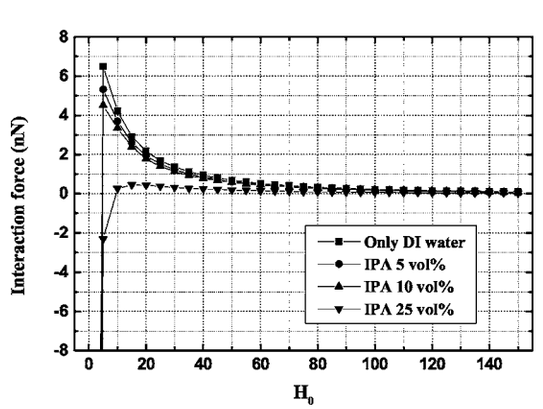

Figure 7. DLVO total interaction force between a silica particle and the Si wafer surface.

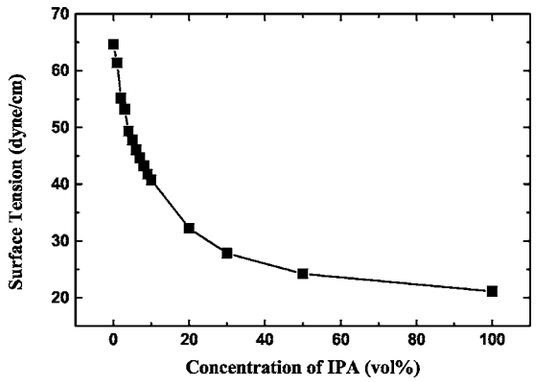

Figure 8. Surface tension of IPA and DI water mixing solutions as a function of IPA concentration.

Figure 8 shows the variation of surface tension of IPA solutions as a function of IPA concentration (by volume) in DI water at the air/liquid interface. The surface tension quickly decreased from 72 to 27 dynes/cm when the IPA concentration was increased to 30 vol %. The presence of IPA in DI water causes a surface excess[17] of IPA molecules at the air–liquid interface. This indicates that IPA is very active at the air–liquid interface at lower concentrations. Gibbs surface excess (Γ) of IPA at the air/solution interface was calculated based on the surface tension of IPA, which can be defined as shown in Eq. 6

$$\Gamma_{IPA} = -\frac{1}{RT}\frac{d\gamma}{d\ln C_{IPA}} = -\frac{C_{IPA}}{RT}\frac{d\gamma}{dC_{IPA}} \quad [6]$$

where R is the constant (8.314 J/mol K), T is absolute temperature (K), and C_{IPA} is molar concentration of IPA (M). The values of $d\gamma/dC_{IPA}$ were calculated from the data of surface tension and molar concentration of IPA in DI water. Table II summarizes the calculated values of $d\gamma/dC_{IPA}$ at different concentrations of IPA.

Figure 9 shows the surface excess of IPA at the air–liquid interface as a function of IPA concentration. The highest surface excess value was calculated at 20% by volume. This indicates that a lower concentration of IPA may play an important role in wafer cleaning and drying. As the wafer passes through the IPA/solution interface, the magnitude of IPA surface excess directly affects the difference in surface pressure at the wafer–air–liquid interface. The role of IPA surface excess was investigated by drying wafers in precontaminated IPA solutions with silica particles. Figure 10 shows the number of contaminated silica particles as a function of the IPA concen-

Table II. The molar concentration of IPA, surface tension, and the calculated values of $d\gamma/dC_{IPA}$ at different concentrations of IPA.

Concentration of IPA (vol %)	Concentration of IPA (M)	Surface tension (dyne/cm)	$d\gamma/dC_{IPA}$
0	0	72	−81.06409
5	0.65427	47.83	−11.24487
10	1.30854	40.79	−8.65373
20	2.61707	32.26	−4.95647
30	3.92561	27.84	−2.37872
50	6.54269	24.25	−0.92431
100	13.08537	21.15	−0.4746

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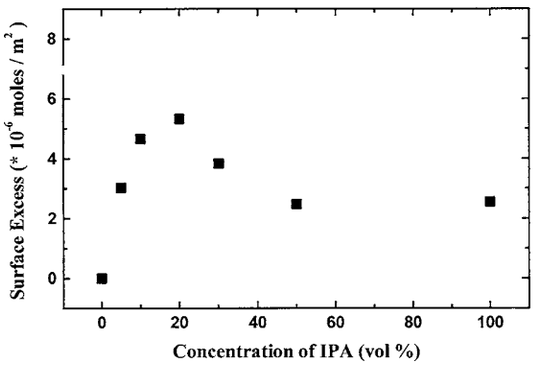

Figure 9. Surface excess of IPA at the air/IPA solution interface.

tration. Fewer particles were deposited in the 5 and 10 vol % IPA solutions than in DI water and in higher concentration IPA solutions.

Although the zeta potential, AFM adhesion forces, and the interaction force indicate a stronger attraction between silica particles and the Si wafer with increasing IPA content in DI water, a lower particle addition was measured at IPA concentrations lower than 10%. This may indicate that the surface pressure caused by the surface tension gradient on the wafer surface is more dominant than the van der Waals and electrostatic forces at concentrations of IPA lower than 10%. However, higher IPA concentrations showed much higher particle addition on silicon wafers when the wafers were withdrawn from solutions. This indicates that lower concentrations of IPA may play an important role in wafer cleaning and drying.

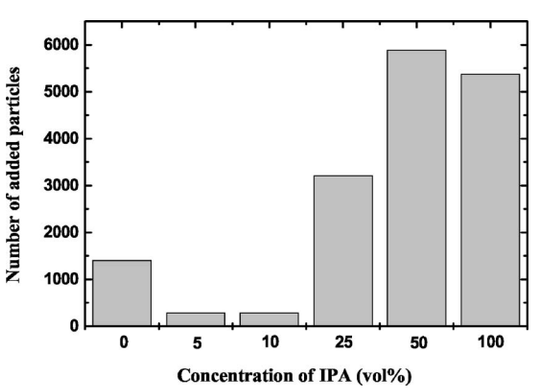

Figure 10. The number of silica particles added when silicon wafers were dried in IPA solutions with silica particles.

Conclusions

The dielectric constant of IPA solutions was observed to linearly decrease as a function of IPA concentration in water. The viscosity of IPA solutions increased up to a 50% IPA concentration, however, further increases of IPA decreased viscosity. The zeta potential of silica and silicon particles in IPA solutions approached a neutral value as the IPA content increased to 50%. The size of particles increased linearly with decreasing IPA concentrations due to the decrease in the zeta potential of particles. When IPA was added to DI water, the adhesion force of a silica particle on a silicon wafer increased and reached a plateau at an IPA concentration of 25%. Surface excess was calculated based on the surface tension of the IPA solutions and was found to reach a maximum at around 20% IPA concentration. At lower concentrations of IPA, less particle contamination was observed on silicon wafers from IPA solutions during drying.

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